IONIZING COLLISIONS OF METASTABLE HELIUM ATOMS IN GASES

By

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CHAPTER I

INTRODUCTION

The importance of investigating molecular interactions as a means of understanding chemical reactions has long been recognized. The usual method of obtaining such information has been to relate bulk properties such as viscosity and virial coefficients to the intermolecular forces on which they depend.[1] The advent of scattering experiments supplied a much more satisfactory tool, allowing the interactions of individual particles to be studied directly rather than through averaged properties. Only through such observation of single collisions will the true nature of chemical reactions ever be completely understood.

Collisions are classified as elastic if the particles survive the collision without exchange of internal energy, and inelastic if such a transfer takes place. The object of a scattering experiment is usually to obtain a cross section, which is a measure of the probability for a particular type of collision, e.g., elastic or inelastic, to occur. Elastic and total cross sections have been investigated by many workers using molecular beam methods. For example, Broadway[2] studied the scattering of a beam of alkali atoms by a perpendicular beam of mercury atoms. Mais[3] and others[4,5] observed total cross sections for scattering of alkali atom beams in various gases. In recent years much progress has been made by Amdur[6] in using beam techniques to determine the force law between relatively high velocity atoms and molecules. More recently,

Smith and Muschlitz[7] have determined total cross sections for collisions of thermal energy metastable atoms in various gases.

For a chemical reaction to occur, the reactant particles must undergo an inelastic collision. In many chemical reactions, the energy transferred on collision is in the form of excitation energy. Several types of inelastic collisions between an excited atom and another particle are possible, e.g.:

$$X^* + Y \longrightarrow X + Y + \text{k.e.} \qquad \text{(I.1)}$$

$$X^* + Y_2 \longrightarrow X + Y_2' + \text{k.e.} \qquad \text{(I.2)}$$

$$X^* + Y \longrightarrow X + Y^* \pm \text{k.e.} \qquad \text{(I.3)}$$

$$X^* + Y \longrightarrow X + Y^+ + e^- + \text{k.e.} \qquad \text{(I.3)}'$$

$$X^* + Y_2 \longrightarrow X + Y + Y + \text{k.e.} \qquad \text{(I.3)}''$$

$$X^* + Y_2 \longrightarrow XY' + Y + \text{k.e.} \qquad \text{(I.4)}$$

The first of these represents the conversion of electronic excitation energy to kinetic energy; the second, conversion to vibration in a diatomic molecule. Eq. (I.3) represents transfer of excitation energy between particles; and Eq. (I.4) chemical reaction between an excited atom and a diatomic molecule. Special cases of Eq. (I.3) include Eq. (I.3)', in which the excitation energy of X* exceeds the ionization potential of Y, and Eq. (I.3)'', in which a molecule, Y_2, is excited to a repulsive state and dissociation occurs. In Eq. (I.4) the resulting molecule, XY, may not only be vibrationally excited but may also be electronically excited or even ionized if X* has sufficient energy.

Reaction (I.1) has been found to occur very seldom,[8] and there is good theoretical justification to substantiate this.[9] The probability of Reaction (I.2) should also be very small if the collision time is short compared with the period of vibration, in accordance with the Frank-Condon

principle. On the other hand, for slow or adiabatic collisions the probability of the latter process must be considered in terms of the dissociation of the collision complex, XY_2. Reaction (I.3) can be a highly probable process if there exists an energy level for Y close to the excitation energy of X*. An example is the excitation of thallium to various excited states by collision with excited mercury atoms in a mixture of the two vapors:[8]

$$Hg(^3P_1) + Tl(^2P_{1/2}) \longrightarrow Hg(^1S_0) + Tl^* + k.e. \quad (I.5)$$

Reaction (I.4) is rare, a few examples having been observed in photochemical investigations.[10]

This dissertation concerns the measurement of ionization cross sections for collisions of metastable helium atoms in argon, krypton, xenon, hydrogen, oxygen, nitrogen, and carbon monoxide. Some of the atoms in gaseous helium are excited to both the 2^1S and 2^3S metastable states by electron bombardment. An atomic beam of the helium atoms at thermal energy is then formed and allowed to enter a collision chamber in which a gas is introduced at low pressure (ca. 10^{-3} mm.). The elastically scattered metastable atoms, as well as those "unscattered," are detected by measuring the electron current ejected by the excited atoms when they strike a metal surface. The ions formed by the inelastic collisions of type (I.3)' are observed as a separate current. Since the method of detection is insensitive to particles in the ground state, there is no interference from the normal helium atoms in the beam.

CHAPTER II

THEORY

Several general references are available on scattering theory[11,12] and on molecular beams.[13,14,15,16] The pioneering molecular beam experiment was made in 1911 by Dunoyer,[17] who produced a beam of sodium atoms and verified that the atoms described rectilinear paths in an evacuated tube. The technique of molecular beam production was later developed almost entirely through the experiments of Stern and his collaborators.[18,19] The formation of a beam of unidirectional atoms or molecules can be achieved by allowing the particles in the gaseous state to pass through a system of collimating slits. In order to have collision-free rectilinear motion in the beam rather than turbulent flow, the diameter of the source aperture must be smaller than the mean free path of the particles in the source. To observe collision cross sections, it is further required that the pressure of the gas in the collision chamber be low enough so that only single collisions occur.

The 2^3S_1 and 2^1S_0 states of helium are metastable with respect to electric dipole radiative decay to the 1^1S_0 ground state. The transition from the triplet state (19.82 ev. above the ground state) is forbidden by the selection rules $\Delta S = 0$ and $\Delta \ell = \pm 1$; that from the singlet state (20.61 ev.) is forbidden by the rules $\Delta \ell = \pm 1$ and $J = 0 \not\longrightarrow J = 0$. Decay to the ground state is possible, however, by processes other than ordinary electric dipole radiation. Among these are magnetic dipole

radiation and double photon emission. But the probabilities for the occurrence of the latter processes are quite low compared to that for electric dipole radiation; hence the lifetimes of metastable atoms in free space are quite long in comparison with non-metastable excited states. For helium the metastable lifetimes are of the order of 10^{-1} seconds,[20] as compared to 10^{-8} seconds for ordinary excited states. For a beam of helium atoms 10 cm. in length, the time of travel required at room temperature is about 10^{-4} seconds. Thus there would be no appreciable loss in intensity of the metastable atoms in a beam of this length.

Numerous investigations have been made on the excitation of helium to its metastable states by electron impact. Maier-Leibnitz[21] measured the total excitation cross sections for energies up to 28 ev., by passing a beam of electrons through helium gas and observing the variation in the electron current as a function of energy. Reder,[22] Abdelnabi,[23] and others found good agreement between discharge parameters calculated from his results and experimentally observed values. Dorrestein[24] studied the total excitation of helium to the metastable levels, using an electron beam with half of the electrons in a 0.25 volt energy range. Shulz and Fox[25] obtained a much better resolution (0.1 volt spread in energy) using the retarding potential difference method.[26] The results of the latter two investigations agree quite well near threshold, the difference being attributable to the different energy spreads. Frost and Phelps[27] have combined the results of the above investigations and others into a complete and consistent picture, arriving at excitation functions for all excited states of helium over an energy range from threshold to

45 ev. From these they then calculated the resultant populations of the 2^1S and 2^3S metastable states as a function of electron energy.

The extraction of an electron from a metal surface by a metastable atom was first established in 1924 by Webb[28] for mercury atoms incident on a nickel surface. In further investigations Sonkin[29] showed the phenomenon to be very complex, and estimated that the maximum efficiency of emission was not greater than a small percentage. For metastable atoms of rare gases, however, much higher efficiencies have been observed. Oliphant[30] made a comprehensive study of electron ejection by helium metastables; however, this did not include a measurement of absolute yield. Dorrestein[24] reported values of 0.24 and 0.48 for the ejection efficiencies of the 2^3S and 2^1S states of helium respectively on a platinum surface. Stebbings[31] obtained a value of 0.29 for the ejection efficiency of 2^3S atoms on a gold surface. Hasted and Mahadevan,[32] using Stebbings' value of 0.29 for a gas-contaminated gold target as a standard, obtained for the efficiency of 2^3S helium on platinum values of 0.26 for a contaminated surface and 0.25 for an atomically clean surface. Studies using molybdenum and tungsten as targets also indicated a rise in electron yield with gas contamination of the surface.

Hagstrum[33] and Varnerin[34] have indicated that the electron ejection from metastable atoms and from the corresponding ions should be largely indistinguishable. According to this theory, both the singlet and triplet helium metastables would be converted into ions at an appreciable distance from the surface. An ion so formed would then undergo an Auger transition resulting in the production of a free electron and the neutralization of the ion. This mechanism would predict equal values of

the ejection efficiency for both metastable states, as well as for the ion, since the nature of the particle at the time it becomes involved in an Auger process would not depend on its nature at large distances from the metal. This was supported by Molnar,[35] who found approximately equal yields for ejection by argon ions and metastables on tantalum and molybdenum surfaces. Furthermore, a reinterpretation by Phelps[36] of Dorrestein's data, on the basis of the latest values for the metastable excitation functions, leads to the value 0.24 for the ejection efficiency of both 2^1S and 2^3S helium on platinum. However, the results of Hasted[32] for 2^3S helium atoms on molybdenum and tungsten do not agree well with those of Hagstrum[37] for helium ions on the same surfaces. A method of using a modification of the present apparatus to determine the separate ejection efficiencies of 2^1S and 2^3S helium directly will be discussed in Chapter IV.

At sufficiently low scattering gas pressures, the intensity of ions produced by collisions of type (I.3)', I_+, is given by:

$$I_+ = I_0 \left(1 - e^{-\bar{\sigma}_i N \ell p}\right) \qquad \text{(II.1)}$$

where: $I_0 = I_{01} + I_{03}$ is the total metastable atom intensity entering the scattering region, I_{01} representing singlets and I_{03} triplets; $\bar{\sigma}_i$ is the average ionization cross section in cm^2 for a beam of given composition; $N = 3.536 \times 10^{16}$ = the number of atoms per cm^3 at 0 degrees C. and 1 mm. pressure; ℓ is the length of the scattering region; and p is the pressure in mm. Hg corrected to 0 degrees C. Rearranging Eq. (II.1) and taking logarithms:

$$\bar{\sigma}_i N \ell p = \ln \frac{I_0}{I_0 - I_+} = \ln r \qquad \text{(II.2)}$$

The value r as a function of scattering gas pressure may be studied, and the cross section, $\bar{\sigma}_i$, may then be found from the slope of a plot of log r versus p.

The average ionization cross section is defined by:

$$\bar{\sigma}_i = \frac{\sigma_{i1} I_{01} + \sigma_{i3} I_{03}}{I_{01} + I_{03}} = \frac{\sigma_{i1} R + \sigma_{i3}}{R + 1} \qquad \text{(II.3)}$$

where: σ_{i1}, represents the ionization cross section for singlet metastables; σ_{i3} that for triplets; and $R = \frac{I_{01}}{I_{03}}$. Since the composition of the beam and hence the value of R varies with the electron energy in the source, $\bar{\sigma}_i$ may be studied as a function of electron energy to yield separate values for σ_{i1} and σ_{i3}. Rearranging Eq. (II.3):

$$(R + 1)\bar{\sigma}_i = \sigma_{i1} R + \sigma_{i3} \qquad \text{(II.4)}$$

A plot of $(R + 1)\bar{\sigma}_i$ versus R thus yields a straight line with a slope equal to σ_{i1} and intercept on the ordinate equal to σ_{i3}.

CHAPTER III

DESCRIPTION OF APPARATUS

The molecular beam apparatus used to make the ionization cross section measurements is essentially the same as that described by Smith and Muschlitz.[7] As shown in Figure 1, it consists of four vacuum chambers: the atom source, fore chamber, post chamber, and scattering chamber. An atomic beam is produced by introducing gas through a capillary leak into the source at room temperature and allowing it to effuse through the first defining hole, H_1, into the fore chamber. Some of the atoms are excited before leaving the source region by an electron beam which passes directly behind H_1. The electron beam is produced by thermionic emission from a thoriated iridium filament, and is confined by a magnetic field of approximately 200 gauss produced by the magnets, D. A potential applied across plates E in the fore chamber deflects from the beam any charged particles that are produced in the source. The beam entering the post chamber through the second defining hole, H_2, is therefore composed of metastable atoms and normal atoms. It then continues into the scattering chamber through a hole in the cylindrical can, G, which separates the scattering region from the post chamber. A magnetically operated shutter, S, placed directly behind H_2, allows the beam to be interrupted to obtain a zero reading. Fast mercury pumps maintain pressures below 10^{-5} mm. in the fore and post chambers.

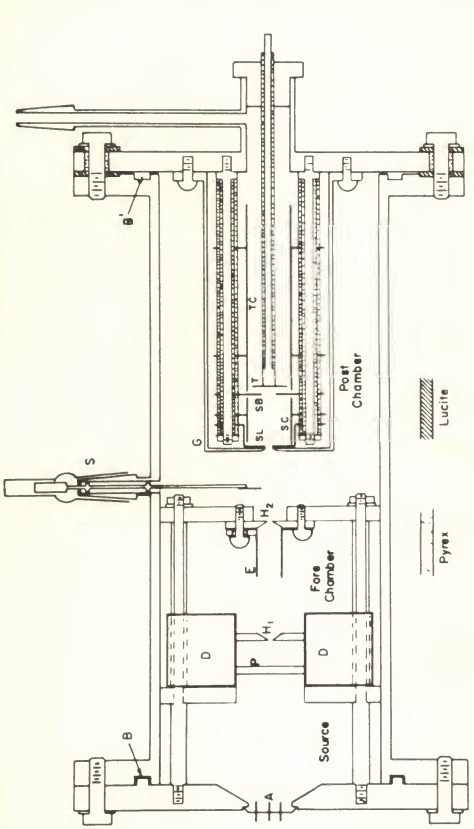


Figure 1. Cross Section of Apparatus

Cylindrical symmetry is maintained throughout the scattering region. Dimensions of the scattering elements are given in Table 1. The scattering elements have been heavily gold plated, to obtain surfaces having the same electron ejection efficiency. The beam entering through the hole in can G passes through a larger hole in the scattering cylinder lid, SL. The elastically scattered metastable atoms are then detected at the scattering cylinder, SC, and the scattering cylinder bottom, SB; and the unscattered metastable atoms at the target, T. The ions produced by inelastic collisions of type (I.3)' are drawn by a suitable potential to the lid, SL, and detected there. The scattering path length, ℓ, is defined as the horizontal distance between the plates SL and SB.

Table 1

Dimensions of Scattering Elements

Length of Scattering Region	2.17 cm.
Diameter of Scattering Cylinder	1.91 cm.
Diameter of Hole in Scattering Cylinder Lid	0.10 cm.
Diameter of Hole in Scattering Cylinder Bottom	0.11 cm.

Current measurements are made by means of a Cary Instruments vibrating-reed electrometer. Figure 2 shows a schematic diagram of the apparatus including the electric circuit. The mercury-pool switch used previously[7] has been eliminated by using two electrometers, one connected to T and the other to SL. If the other electrodes (SC and SB) are made negative, electron currents are read on T and SL, the sum of which, i_s, represents the electrons ejected from SC and SB by elastically scattered metastables plus the electrons formed in ionizing collisions.

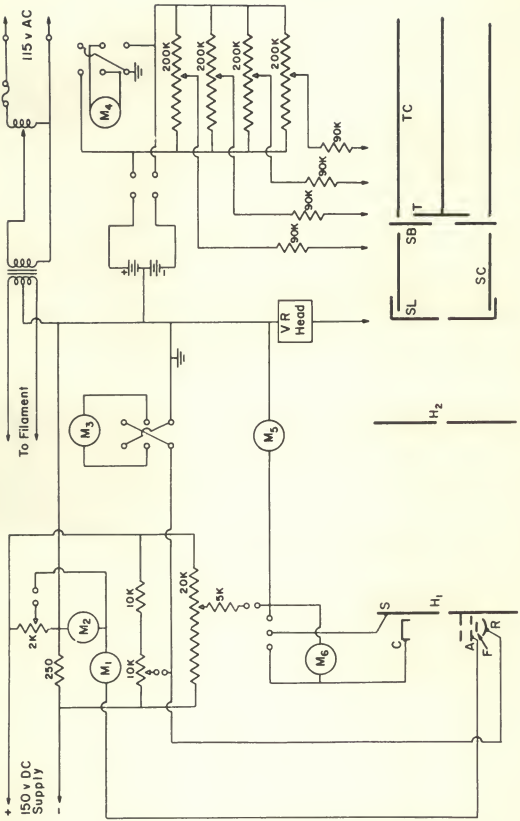


Figure 2. Schematic Diagram of Apparatus

If SC and SB are made positive, a positive current is read on SL, i_+, representing the positive ions produced; and a positive current is read on T, i_T, representing electrons ejected from T by unscattered metastable atoms. The total current, i_0, is then obtained by adding i_T and i_S, without regard to sign.

In terms of the currents i_+ and i_0, the total metastable atom intensity entering the scattering region is given by:

$$I_0 = i_+ + \frac{i_0 - i_+}{\bar{\gamma}} \qquad \text{(III.1)}$$

where:

$$\bar{\gamma} = \frac{\gamma_3 I_{03} + \gamma_1 I_{01}}{I_{03} + I_{01}} \qquad \text{(III.2)}$$

is the average electron ejection efficiency. It is readily seen that if γ_3 and γ_1 are assumed equal Eq. (III.2) reduces to this common value. The ions are assumed to be collected with 100 per cent efficiency, hence $I_+ = i_+$. Utilizing Eq. (III.1):

$$r = \frac{I_0}{I_0 - I_+} = \frac{\bar{\gamma}\, i_+}{i_0 - i_+} + 1 \qquad \text{(III.3)}$$

The values of r to be used in connection with Eq. (II.2) may therefore be obtained by using the appropriate $\bar{\gamma}$ and the experimentally determined currents, i_+ and i_0.

The use of both electrometers simultaneously was originally prohibited, since a capacitative coupling between the instruments caused periodic output fluctuations which made accurate readings impossible. Hence, readings could be taken only with one instrument on at a time. A single set of measurements was thus greatly time-consuming, since a warming-up period was required for each instrument after having been

previously turned off. This difficulty has been obviated by means of a "master-slave" modification supplied by the manufacturer, through which the oscillator of one of the instruments is used to drive the reeds in both electrometers. In this way both electrometers can now be operated at the same time, greatly decreasing the time required for each set of readings. Data obtained since the introduction of the modified circuit agree well with those obtained under the previous conditions.

An auxiliary vacuum system used for gas manipulation and pressure measurements is shown in Figure 3. The upper manifold is used for pressure measurements either with ion gauge, I_1, or the McLeod Gauge. The two lower manifolds are used to introduce gases into the source and the scattering region. A capillary leak, L_1, and a needle valve, L_2, are used to decrease the pressure from the bulbs, B, to about 10^{-1} mm. and 10^{-3} mm. in the source and scattering region respectively. Scattering pressures are measured with the McLeod Gauge, which had been calibrated previously.[7]

Helium was introduced into the system through a trap which contained degassed charcoal at liquid air temperatures. It was estimated that impurities in this gas amounted to less than one part in 10^3. The gas samples used in the scattering region were taken from flasks of reagent-grade gas supplied by the Air Reduction Sales Company with the exception of hydrogen, which was introduced in the same manner as helium. Reported impurities for these flasks, determined by mass spectrographic analysis, were in all cases less than one part in 10^4. The apparatus itself was kept filled with helium to one atmosphere between periods of operation, thus preventing the adsorption of foreign gases on the walls of the apparatus.

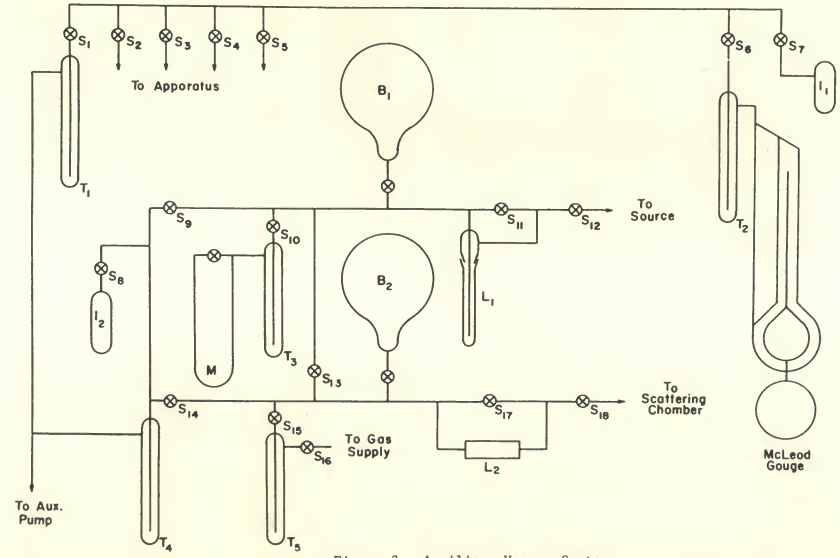


Figure 3. Auxiliary Vacuum System

CHAPTER IV

RESULTS AND DISCUSSION

In order to determine the proper potential to be used on the detecting electrodes for the ionization measurements, studies were made of the variation of i_{SL}, the current to the scattering lid (SL in Figure 1), with drawout potential. Figure 4 is a plot of i_{SL} versus drawout potential for argon, in which a plateau appears from about 10 to 20 volts. In this region the potential difference is sufficient to prevent electron ejection from the electrodes at negative potential and, at the same time, insufficient to accelerate electrons to an energy where they themselves would ionize the gas. From these studies it was found that a potential of 13 volts would be satisfactory for all the gases investigated.

Figure 5 is a plot of log r in argon versus pressure for three electron energies. The curves are displaced along the abscissa for clarity. The method of least squares was used to determine the best straight line passing through the origin for each set of points. The original data may be found in the Appendix, along with calculated values of $\bar{\sigma}_i$. The standard deviations of the slopes are also included to indicate the probable experimental error in the values of the cross sections found. For the calculation of log r, Frost and Phelps' values[27] for $R = I_{01}/I_{03}$ were used, and the value 0.29 was used for both γ_1 and γ_3. Since there is no appreciable change or apparent trend in the slope with increasing electron energy, it may be concluded that the cross

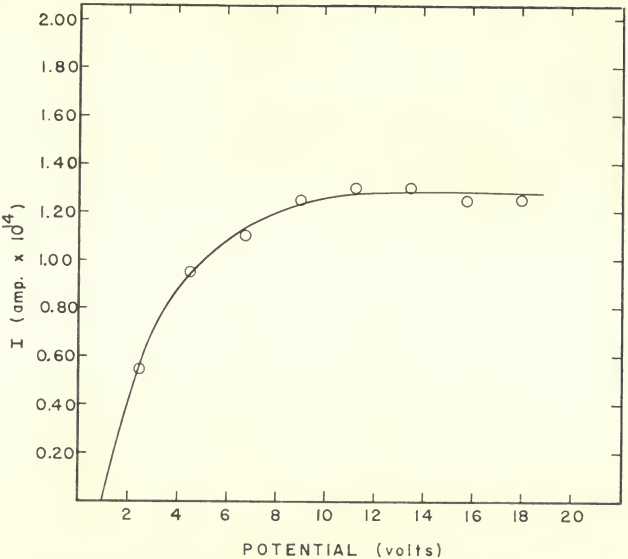


Figure 4. i_{SL} Versus Drawout Potential for Argon

sections for the two metastable species in argon are essentially the same. Hence a resolution of the data into separate values for σ_{i1} and σ_{i3} was not warranted, and a simple averaging was employed to determine a single value for both cross sections. This treatment yields a value of 8 ± 0.5 A^2 for the cross section for ionization of an argon atom by collision with either metastable helium atom.

Plots of log r versus pressure for krypton, xenon, hydrogen, oxygen, nitrogen, and carbon monoxide are shown in Figures 6 through 11. These data are quite similar to the argon data and are treated in the same manner. It is seen that the only gas which exhibits an apparently significant trend in $\bar{\sigma}_i$ with electron energy is hydrogen. For this case, then, a plot of $(R + 1)\bar{\sigma}_i$ versus R was made, from which the values $\sigma_{i3} = 3 \pm 0.5$ and $\sigma_{i1} = 2 \pm 0.5$ were found.

The ionization cross sections for all the gases investigated are reported in Table 2. In column three of this table are shown the energetically possible processes for each gas, the excess energy, ΔE, being given in column four. The ΔE values were obtained using the data for ionization potentials, dissociation energies, and electron affinities listed in Table 3.

Since the process of ionization in collisions of metastable particles was first discovered by Penning,[38] very few measurements of cross sections for such processes have been made. Biondi[39] obtained a value of 1 A^2 for the ionization cross section of metastable helium in argon, an order of magnitude less than that found in the present work. This result pertains to a mixture of singlet and triplet metastables of unknown composition, and was arrived at by studying the variation of electron density in a gaseous discharge via microwave techniques.

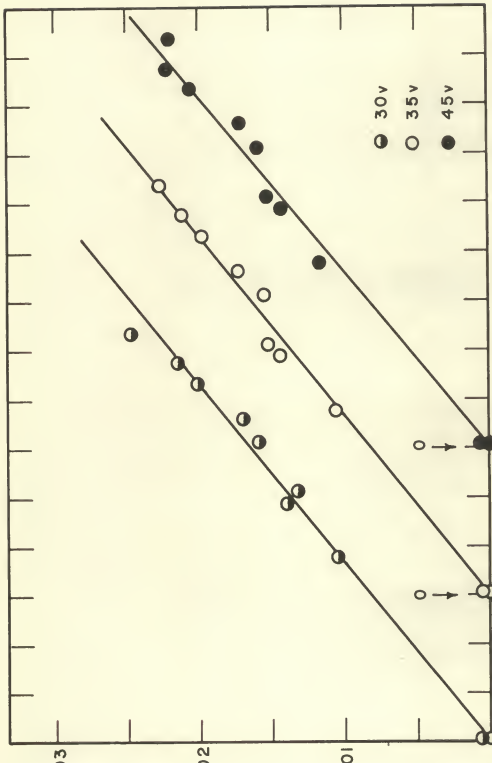


Figure 5. Log r in Argon Versus Pressure for Three Electron Energies

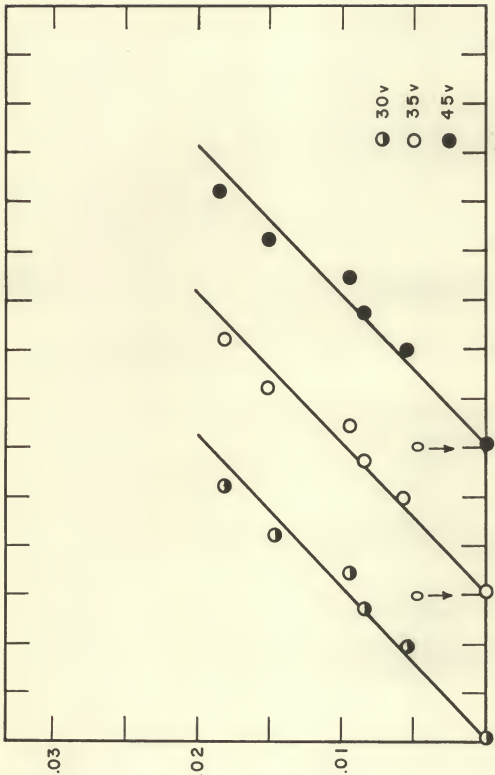


Figure 6. Log r in Krypton Versus Pressure for Three Electron Energies

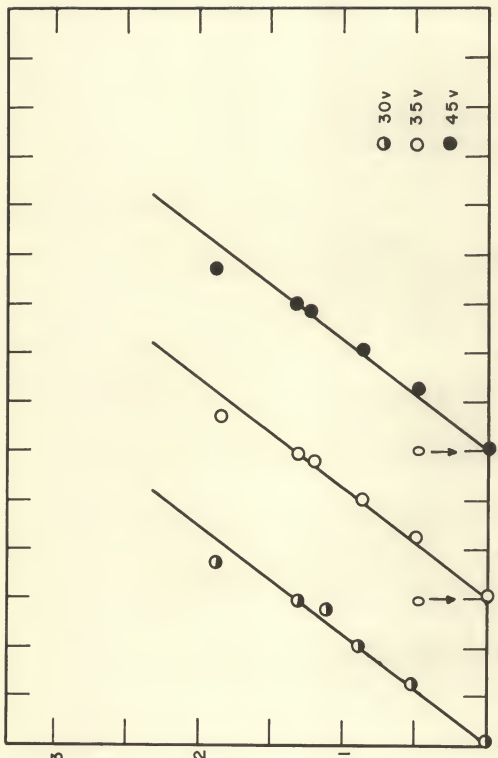


Figure 7. Log r in Xenon Versus Pressure for Three Electron Energies

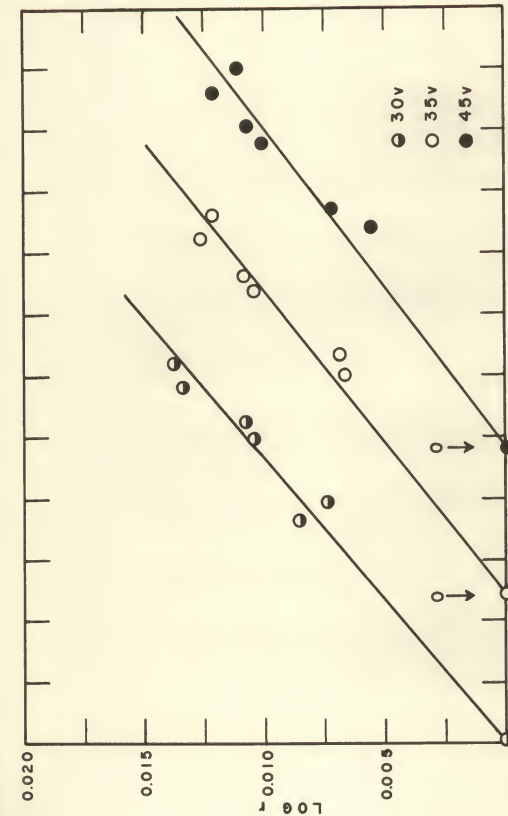


Figure 8. Log r in Hydrogen Versus Pressure for Three Electron Energies

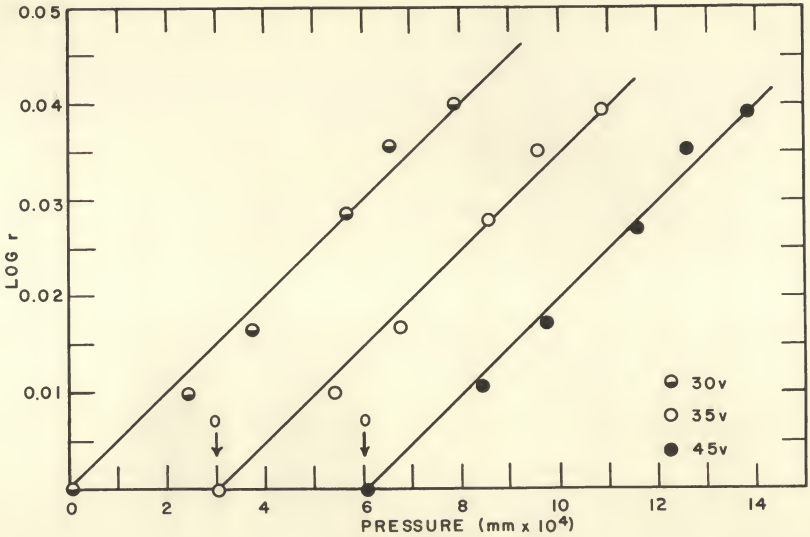


Figure 9. Log r in Oxygen Versus Pressure for Three Electron Energies

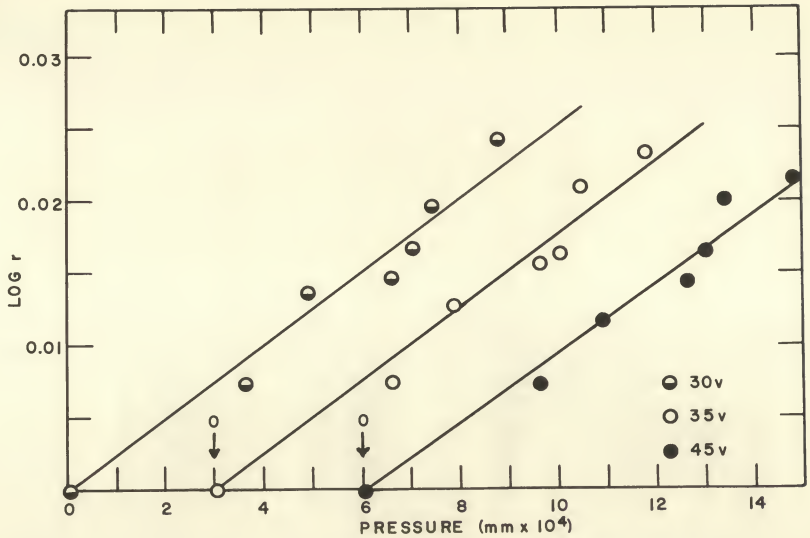


Figure 10. Log r in Nitrogen Versus Pressure for Three Electron Energies

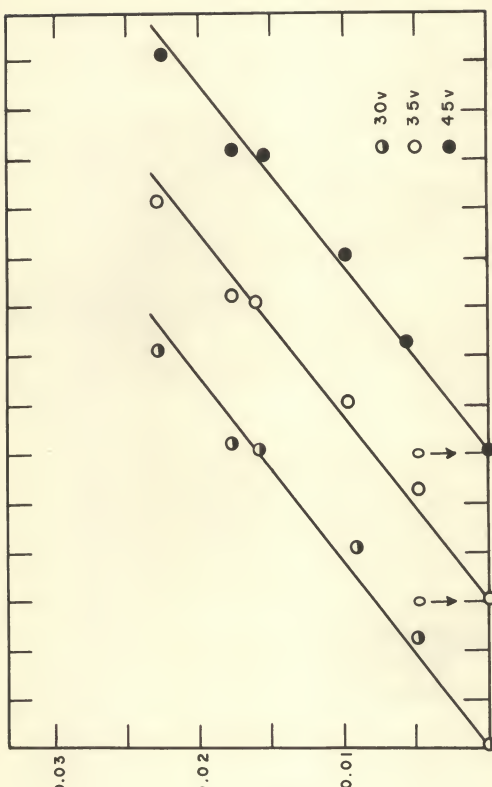


Figure 11. Log r in Carbon Monoxide Versus Pressure for Three Electron Energies

Table 2. Ionization Cross Sections

Metastable Atom	Gas	Possible Ions Formed	ΔE(ev.)	σ_i(A^2)	σ_i/σ_i argon	
					This work	Jesse and Sadauskis[47]
$He(2^3S)$	$A(^1S_0)$	$A^+(^2P)$	-4.06	8 ± 0.5		
$He(2^1S)$		$A^+(^2P)$	-4.85	8 ± 0.5	1.0	1.0
$He(2^3S)$	$Kr(^1S_0)$	$Kr^+(^2P)$	-5.82	9 ± 2		
$He(2^1S)$		$Kr^+(^2P)$	-6.61	9 ± 2	1.1	2.5
$He(2^3S)$	$Xe(^1S_0)$	$Xe^+(^2P)$	-7.69	12 ± 3		
$He(2^1S)$		$Xe^+(^2P)$	-8.48	12 ± 3	1.5	3.1
$He(2^3S)$	$H_2(^1\Sigma g^+)$	$H_2^+(X^2\Sigma g^+)$	-4.40	3 ± 0.5		
		$H^+ + H(^2S)$	-1.75			
		$H^+ + H^-(^1S)$	-2.50			
		$HeH^+(X^1\Sigma) + H(^2S)$	-3.6			
		$HeH^+(X^1\Sigma) + H^-(^1S)$	-4.4			
$He(2^1S)$		$H_2^+(X^2\Sigma g^+)$	-5.19	2 ± 0.5	0.3	0.3
		$H^+ + H(^2S)$	-2.54			

Table 2. Continued

Metastable Atom	Gas	Possible Ions Formed	ΔE(ev.)	σ_i(A^2)	σ_2/σ_1 argon	
					This work	Jesse and Sadauckis[47]
		$H^+ + H^-(^1S)$	-3.29			
		$HeH^+(X^1\Sigma) + H(^2S)$	-4.4			
		$HeH^+(X^1\Sigma) + H^-(^1S)$	-5.2			
$He(2^3S)$	$O_2(^3\Sigma_g^-)$	$O_2^+(X^2\Pi_g)$[a]	-7.6	14 ± 1		
		$O^+(^4S) + O(^3P)$	-1.13			
		$O^+(4S) + O^-(^2P)$	-2.59			
$He(2^1S)$		$O_2^+(X^2\Pi_g)$[a]	-8.4	14 ± 1	1.8	
		$O^+(4S) + O(^3P)$	-1.92			
		$O^+(4S) + O^-(^2P)$	-3.38			
		$O^+(4S) + O^*(^1D)$	+0.05			
		$O^{+*}(^2D) + O^-(^2P)$	-0.05			
$He(2^3S)$	$N_2(^1\Sigma_g^+)$	$N_2^+(X^2\Sigma_g^+)$[a]	-4.24	7 ± 1		
$He(2^1S)$		$N_2^+(X^2\Sigma_g^+)$[a]	-5.03	7 ± 1	0.9	0.9

Table 2. Continued

Metastable Atom	Gas	Possible Ions Formed	ΔE(ev.)	σ_i(A^2)	σ_i/σ_i argon	
					This work	Jesse and Sadauskis[47]
He(2^3S)	CO($^1\Sigma^+$)	$CO^+(X^2\Sigma^+)$[a]	-5.81	7 ± 1		
		$C^+(^2P) + O^-(^2P)$	-0.42			
He(2^1S)		$CO^+(X^2\Sigma^+)$[a]	-6.60	7 ± 1	0.9	
		$C^+(^2P) + O^-(^2P)$	-1.21			

[a]Several excited electronic states of the molecular ion are also possible.

Table 3. Energy Values for Calculation of ΔE

Ionization potentials, Dissociation energies, and Electron Affinities	Energy (ev.)	Reference
IP(A)	15.756	Herzberg[41]
IP(Kr)	13.996	Herzberg[41]
IP(Xe)	12.127	Herzberg[41]
IP(H_2)	15.422	Herzberg[42]
IP(H)	13.595	Herzberg[41]
IP(O_2)	12.2	Herzberg[42]
IP(O)	13.615	Herzberg[41]
IP(N_2)	15.576	Herzberg[42]
IP(CO)	14.01	Herzberg[42]
IP(C)	11.265	Herzberg[41]
D(H_2)	4.476	Herzberg[42]
D(HeH^+)	1.9	Evett[43]
D(O_2)	5.080	Herzberg[42]
D(CO)	9.605	Hagstrum[44]
EA(H)	0.747	Henrich[45]
EA(O)	1.465	Branscomb[46]

Phelps[40] utilized optical absorption measurements from a pulsed discharge in a helium-argon mixture to obtain values of 3 A^2 and 11 A^2 for σ_{i3} and σ_{i1} respectively. The average of these values agrees well with that reported here, but it is difficult to interpret a large difference in the cross sections such as he reports.

Jesse and Sadauskis[47] have studied the increase in ionization produced by alpha particles in helium caused by minute quantities of various gases. From their results relative ionization cross sections were calculated. Since the metastable helium mixtures obtained in these investigations were calculated to consist of about 90 per cent singlets, the resulting cross sections for all practical purposes correspond to σ_{i1}. In column seven of Table 2 are listed Jesse and Sadauskis' values of ionization cross sections relative to argon for singlet helium metastables in Kr, Xe, H_2, and N_2. In column six are the corresponding ratios found in the present work for all the gases investigated. For the inert gases some discrepancy is seen; however, the trend is in the same direction in both cases, namely an increase in cross section with atomic weight. Excellent agreement is found for H_2 and N_2.

Little theoretical work has been done on ionization collisions such as those listed in Table 2. A reaction of type (I.3)':

$$X^* + Y \longrightarrow X + Y^+ + e^- + \text{k.e.} \qquad \text{(I.3)'}$$

is generally considered to be one of exact resonance, for the excess energy may be carried off by the ejected electron so that the energy of relative motion of the nuclei involved is not altered.[48] If this is the case, the value of the excess energy, ΔE, would have little effect on

the cross section, so long as the reaction in question is energetically possible. For a collision such as:

$$He^* + H_2 \longrightarrow He + H^+ + H^- + k.e. \qquad (IV.1)$$

there is no electron produced to carry off the excess energy. The resonance concept is not considered to come into play in the case of diatomic molecules, however, since the surplus energy here is likely converted into molecular vibration, which then leads to dissociation if the energy is great enough. This type of reaction is usually interpreted in terms of interactions of the potential energy hypersurfaces pertinent to the collision complex.[48]

Von Roos[49] has recently proposed that the process in Eq. (I.3)' be considered as being intermediate between true resonance collisions and nonresonance collisions. According to this picture only part of the excess energy is carried off by the electron, the remainder going into nuclear motion. This would introduce a relation between σ_i and ΔE, since for nonresonance collisions the probability of reaction decreases with increase in excess energy.[48] Thus, for the sequence argon, krypton, and xenon, the ionization cross section for collisions with metastable helium atoms would be expected to decrease in the order mentioned. This is contrary to the results of the present work, as well as those of Jesse and Sadauskis. Also, a quantum mechanical calculation of the cross section for the reaction:

$$He(2^3S) + He(2^3S) \longrightarrow He(1^1S) + He^+ + e^- + k.e. \quad (IV.2)$$

made on the basis of the semiresonance picture, leads to a value which disagrees by four orders of magnitude with experimental findings.[50]

Finally, data in Von Roos' Table I which seem to support his theory are improperly quoted,[39] hence there appears to be no evidence in its favor.

Atomic size may be the determining factor in the relative values of σ_i for the series: argon, krypton, xenon. For each of these atoms there is only one energetically possible ionization reaction with a metastable helium atom; and the differing values of ΔE should have little effect on these cross sections, as explained in the preceding paragraphs. The diameters of the A, Kr, and Xe atoms according to kinetic theory[51] are 3.64, 4.16, and 4.85 angstroms respectively. Therefore, the increase in cross section going from Kr to Xe might be expected to be somewhat larger than that going from A to Kr. On this basis, the present observations are more consistent than those of Jesse and Sadauskis. Due to the large probable errors in the present results for krypton and xenon, too much significance should not be attached to a quantitative agreement. It is evident, however, that the size of the struck particle is the primary factor in determining the cross section for ionization of the rare gases, rather than the energy excess.

The observed ionization cross sections for the diatomic molecules may be considered in terms of the ionization processes possible in each case. A large number of such processes are energetically possible for H_2, but the small size of the molecule apparently is the overriding factor here. Also, some of the processes listed in Table 2 may be improbable for some reason, such as the absence of any crossing point among the potential energy curves of the corresponding species. For processes involving the formation of the H^- ion, the spin conservation rule[48] should favor the reaction with 2^1S helium over that with 2^3S helium. The fact that σ_{i1} here is not larger than σ_{i3}, but is in fact

apparently smaller, may indicate that these processes do not contribute significantly to the ionization cross section. On the other hand, there is no apparent reason why σ_{i3} should be larger than σ_{i1}.

The cross sections for the ionization of nitrogen and of carbon monoxide are about half that of oxygen. In the case of N_2, ionization accompanied by dissociation is energetically impossible; for CO this type of process is possible only in the case where the O^- ion is formed. The value for the dissociation energy of CO given in Table 3, however, is a doubtful one. A value of 11.108 ev. for D(CO) is given by Gaydon,[52] and there is indirect evidence[53] in its favor. If this value is correct, the reaction with CO to produce C^+ and O^- would actually be energetically impossible for both the singlet and triplet metastable helium atoms. CO would then be on a par with N_2 concerning the number and type of possible ionization processes. This, together with the fact that the sizes of the CO and N_2 molecules are approximately equal,[51,54] would make the observed equal values of σ_i for these two gases seem reasonable.

The large ionization cross sections in the case of oxygen may be explained by the additional processes which are energetically possible here. The absence of any difference between σ_{i1} and σ_{i3} for this gas seems to indicate that the last two processes listed for the collision of 2^1S helium with O_2 are probably not significant. Indeed, these processes would be expected to have a low probability if the Franck-Condon principle holds rigorously in collisions of this type.

Several possible sources of error in these experiments should be considered. There is a small contribution to the current, i_+, by metastable atoms elastically scattered in the backward direction and thus ejecting electrons from the scattering lid, SL. This will make the

final results high; however, the error in neglecting this factor is estimated at no more than 10 per cent, by comparison with results obtained by Smith[7] using the same apparatus for studies of collision cross sections of metastable helium atoms in helium, neon, and argon.

There will also be a small contribution to i_+ due to the ejection of electrons from SL by the positive ions being collected there. Hagstrum[37] has studied the process of electron ejection by rare gas ions on various targets for kinetic energies down to 10 ev. On tungsten, the ejection efficiencies for A^+, Kr^+, and Xe^+ at low kinetic energies were found to be 0.10, 0.05, and 0.02 respectively, and on molybdenum he obtained the corresponding values 0.12, 0.07, and 0.03. Approximately the same values would be expected on a gold target on the basis of relative efficiencies observed for metastable atoms, which are believed to cause electron ejection by the same mechanism as the corresponding ions (pp. 6, 7). Neglecting this factor would then lead to an error of about 10 per cent in the case of argon. The errors for krypton and xenon would, of course, be much lower, and in fact argon probably would exhibit the maximum effect among the gases studied here, since it produces ions of greatest ionization energy (Table 3).

It might be expected that photons resulting from collisions in the scattering chamber would cause some error by photoelectric emission from the metal surfaces, however the contribution of this effect has been shown previously to be negligible.[7] It should also be possible for photons originating from de-excitation of atoms in the source to pass through the defining holes and strike the target, thus contributing to the current, i_T. In attempts to detect a current caused by photons, i_T was found to be reduced to essentially zero for scattering gas pressures

at which the majority of any photons present should still have reached the target. In order to confirm this observation, a thin collodion-film window similar to that described by Stebbings[31] was constructed and mounted on the magnetically operated shutter (S of Figure 1). Such a window should not absorb an appreciable fraction of any photons in the beam. The window was found, however, to be just as effective in stopping the beam as the metal shutter itself.

Another possible source of systematic errors is involved in the uncertainty of the correct values of the ratio of singlet to triplet metastables in the beam, R, and also for the electron ejection efficiencies, γ_1 and γ_3. Of these, the values of Frost and Phelps[27] for R are probably reliable. Also, if the ionization cross sections are approximately equal for both metastable species in a given gas, as indicated in Table 2, the actual values of R have little effect on the results. It may be shown, however, that the values used for γ_1 and γ_3 are extremely critical in calculating ionization cross sections from the experimental data. To illustrate this, the ionization cross sections have been recalculated on the basis of a ratio of 2:1 for $\gamma_1 : \gamma_3$, as was originally reported by Dorrestein.[24] Using $\gamma_1 = 0.6$ and $\gamma_3 = 0.3$, $\bar{\gamma}$ for each electron energy was calculated from Eq. (III.2). Log r was then recalculated from the original data using these values of $\bar{\gamma}$ and $\bar{\sigma}_i$ found in the same manner as described before. A definite trend was now found in the variation of $\bar{\sigma}_i$ with electron energy for each gas, hence a resolution into σ_{i1} and σ_{i3} was carried out according to Eq. (II.4).

Table 4 compares the results of the above treatment with those reported in Table 2. It would be difficult to explain the large differences between σ_{i1} and σ_{i3} which result from assuming a 2:1 ratio for

Table 4. Cross Sections Using Different Values of $\bar{\gamma}$

Metastable Atom	Gas	$\sigma_i(A^2)$ $\gamma_1 = \gamma_3 = 0.29$	$\sigma_i(A^2)$ $\gamma_3 = 0.3$ $\gamma_1 = 0.6$
He(2^3S)	A	8	8
He(2^1S)		8	15
He(2^3S)	Kr	9	9
He(2^1S)		9	18
He(2^3S)	Xe	12	13
He(2^1S)		12	25
He(2^3S)	H_2	3	3
He(2^1S)		2	4
He(2^3S)	O_2	14	14
He(2^1S)		14	27
He(2^3S)	N_2	7	8
He(2^1S)		7	13
He(2^3S)	CO	7	8
He(2^1S)		7	15

$\gamma_1 : \gamma_3$. Also, the case for equal values of γ_1 and γ_3 seems well founded on theoretical grounds (pp. 6, 7). Nevertheless, because of the drastic effect this factor has on the calculated cross sections, it would be most valuable if the question could be settled experimentally. A method whereby this may be done will now be described.

A modification of the present apparatus is now underway which should enable the relative values of the electron ejection efficiencies for 2^1S and 2^3S helium atoms on a gold surface to be determined. In the modified apparatus the beam containing metastable atoms will pass through an inhomogeneous magnetic field. In this field the total angular momentum quantum number for the triplet metastable, J = 1, will be split into three equal components, $M_J = +1, 0$, and -1. The inhomogeneity of the field will then produce a force on those atoms having M_J values of $+1$ and -1, causing them to be deflected from the beam. The resulting metastable beam will then be composed of all the singlets plus one-third of the triplets which were originally in the beam. In the absence of a scattering gas, the total currents detected in the scattering region with the magnetic field off and on, respectively, will be:

Field off: $$i_0 = I_{01}\gamma_1 + I_{03}\gamma_3 \qquad \text{(IV.3)}$$

Field on: $$i_{0F} = I_{01}\gamma_1 + 1/3 I_{03}\gamma_3 \qquad \text{(IV.3)'}$$

The difference is:

$$i_0 - i_{0F} = 2/3 \; I_{03}\gamma_3 \qquad \text{(IV.4)}$$

By measuring these currents, therefore, the quantity $I_{03}\gamma_3$ may be determined. Then by substituting this into Eq. (IV.3) the value of

$I_{01}\gamma_1$ may also be found. Dividing the latter quantity by the former yields:

$$\frac{I_{01}\gamma_1}{I_{03}\gamma_3} = R\,\frac{\gamma_1}{\gamma_3} \qquad \text{(IV.5)}$$

From this, the ratio of $\gamma_1 : \gamma_3$ may be readily calculated at any electron energy by using the appropriate value of R. Since this ratio does not depend on the electron energy, the consistency of Frost and Phelps' values of R as a function of energy may also be checked in this way.

The inhomogeneous magnetic field described above will also allow the determination of separate ionization cross sections for collisions of 2^1S helium and 2^3S helium directly, rather than through the resolution of average cross sections. If this is successful, it should finally be possible to differentiate between the various collision processes by mass spectrometric analysis of the positive ions produced. This would involve the use of a beam of metastable atoms as the ionizing agent in the ion source of the spectrometer rather than the usual electron beam. The resulting mass spectrum would be simpler to interpret than in the electron beam case, since a metastable atom transfers a precisely known amount of energy in a collision--the thermal kinetic energy of the colliding particles being negligible.

CHAPTER V

SUMMARY

A molecular beam method has been employed to measure ionization cross sections for collisions of metastable helium atoms in various gases. A cylindrical beam of thermal energy metastable atoms, produced by electron bombardment of helium gas, was passed through a scattering chamber containing the scattering gas at pressures of the order of 10^{-3} mm. Hg. Ions produced in the gas by inelastic collisions were detected at a metal electrode, and unscattered or elastically scattered metastable atoms were detected by observing the electrons they ejected from metal surfaces. From the ratios of the ion current to the total current, ionization cross sections in A^2, σ_i, were calculated.

Ionization cross sections have been measured for each of the metastable states of helium in argon, krypton, xenon, hydrogen, oxygen, nitrogen, and carbon monoxide. Within the experimental error of the measurements, the cross sections for the 2^1S and 2^3S states of helium were the same in all cases except that of hydrogen. The results have been discussed in terms of energetically possible ionization processes for each gas, the energy excess, ΔE, for these processes, and the size of the scattering atoms or molecules. For the rare gases, the results indicated that the size of the struck particle is the primary factor in determining the cross section for ionization, rather than the energy excess. In the case of the diatomic molecules an additional consideration,

that of the number and type of ionization processes possible, was also found to be important.

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APPENDIX

ORIGINAL DATA

Metastable Helium in Argon, 30 Electron Volts

$p \times 10^4$	i_+	i_T	i_S	i_+/i_0-i_+	log r
0.06	0.05	8.60	1.15	0.0052	0.0006
3.78	0.65	4.80	3.55	0.0844	0.0105
5.12	0.50	2.75	2.50	0.1055	0.0131
6.61	0.90	3.30	4.15	0.1375	0.0170
7.31	0.90	2.60	3.80	0.1637	0.0202
8.34	1.15	2.50	4.35	0.2020	0.0247
0.06	0.00	7.95	----	0.0000	0.0000
4.88	0.85	4.25	4.10	0.1132	0.0140
6.12	0.85	3.40	4.05	0.1287	0.0159
7.74	1.05	2.90	4.15	0.1750	0.0215
	Slope = 27.5 ± 1.0			$\sigma_i = 7.6 \pm 0.3$	

Metastable Helium in Argon, 35 Electron Volts

$p \times 10^4$	i_+	i_T	i_S	i_+/i_0-i_+	log r
0.06	0.05	10.15	1.45	0.0043	0.0005
3.78	0.75	5.60	3.95	0.0852	0.0106
5.12	0.55	2.70	2.30	0.1235	0.0153
6.61	1.10	4.25	4.70	0.1400	0.0173
7.31	0.95	3.00	3.85	0.1610	0.0198
8.34	1.35	3.50	5.15	0.1850	0.0227
0.06	0.00	8.05	----	0.0000	0.0000
4.88	0.90	4.60	4.05	0.1162	0.0144
6.12	0.90	3.80	4.30	0.1250	0.0155
7.74	1.10	3.25	4.25	0.1718	0.0211

Slope = 27.4 ± 0.7 $\qquad \alpha_1 = 7.5 \pm 0.2$

Metastable Helium in Argon, 45 Electron Volts

$p \times 10^4$	i_+	i_T	i_S	i_+/i_0-i_+	log r
0.06	0.05	9.25	1.30	0.0048	0.0006
3.78	0.75	5.25	3.45	0.0943	0.0117
5.12	0.50	2.60	1.95	0.1235	0.0153
6.61	1.00	4.15	4.05	0.1390	0.0172
7.31	0.90	2.95	3.30	0.1681	0.0206
8.34	1.20	3.45	4.45	0.1790	0.0220
0.06	0.00	7.80	----	0.0000	0.0000
4.88	0.90	4.65	4.05	0.1153	0.0143
6.12	0.90	3.95	3.95	0.1286	0.0159
7.74	0.15	3.40	4.10	0.1810	0.0222
	Slope = 28.0 ± 1.0			$\bar{\sigma}_i = 7.7 \pm 0.3$	

Metastable Helium in Krypton, 30 Electron Volts

$p \times 10^4$	i_+	i_T	i_S	i_+/i_0-i_+	log r
0.08	0.00	14.65	----	0.0000	0.0000
1.99	0.55	8.80	4.45	0.0433	0.0054
2.71	0.80	8.00	4.70	0.0672	0.0084
3.44	0.90	7.35	5.40	0.0760	0.0095
4.21	1.25	6.10	5.70	0.1185	0.0147
5.22	1.60	5.60	6.80	0.1480	0.0182
	Slope = 31.9 ± 6.2			$\bar{\sigma}_i = 8.8 \pm 1.7$	

Metastable Helium in Krypton, 35 Electron Volts

$p \times 10^4$	i_+	i_T	i_S	i_+/i_0-i_+	log r
0.08	0.00	14.10	----	0.0000	0.0000
1.99	0.60	9.10	4.50	0.0462	0.0058
2.71	0.85	8.45	4.70	0.0691	0.0086
3.44	0.95	7.75	5.50	0.0773	0.0096
4.21	1.35	6.55	5.80	0.1228	0.0152
5.22	1.65	6.00	6.80	0.1480	0.0182

Slope = 32.5 ± 6.3 $\quad \sigma_i = 8.9 \pm 1.7$

Metastable Helium in Krypton, 45 Electron Volts

$p \times 10^4$	i_+	i_T	i_S	i_+/i_0-i_+	log r
0.08	0.00	13.50	----	0.0000	0.0000
1.99	0.55	8.80	4.10	0.0445	0.0056
2.71	0.80	8.15	4.40	0.0681	0.0085
3.44	0.90	7.60	5.15	0.0759	0.0095
4.21	1.30	6.50	5.45	0.1221	0.0151
5.22	1.65	6.15	6.40	0.1512	0.0186

Slope = 32.5 ± 7.4 $\quad \sigma_i = 8.9 \pm 2.0$

Metastable Helium in Xenon, 30 Electron Volts

$p \times 10^4$	i_+	i_T	i_S	i_+/i_0-i_+	log r
0.08	0.00	13.00	----	0.0000	0.0000
1.28	0.50	8.50	3.90	0.0420	0.0053
2.08	0.85	7.70	4.95	0.0720	0.0090
2.81	1.00	6.85	5.15	0.0909	0.0113
2.97	1.10	6.40	5.05	0.1061	0.0132
3.71	1.50	5.45	5.80	0.1539	0.0189

Slope = 44.6 ± 11.6 $\quad \bar{\sigma}_i = 12.3 \pm 3.2$

Metastable Helium in Xenon, 35 Electron Volts

$p \times 10^4$	i_+	i_T	i_S	i_+/i_0-i_+	log r
0.08	0.00	12.90	----	0.0000	0.0000
1.28	0.50	8.35	4.05	0.0400	0.0050
2.08	0.85	7.95	5.10	0.0697	0.0087
2.81	1.10	7.10	5.30	0.0973	0.0121
2.97	1.15	6.75	5.20	0.1065	0.0132
3.71	1.55	5.90	5.90	0.1512	0.0186

Slope = 44.5 ± 7.5 $\quad \bar{\sigma}_i = 12.3 \pm 2.0$

Metastable Helium in Xenon, 45 Electron Volts

$p \times 10^4$	i_+	i_T	i_S	i_+/i_0-i_+	log r
0.08	0.00	11.95	----	0.0000	0.0000
1.28	0.45	8.50	3.75	0.0382	0.0048
2.08	0.80	7.65	4.65	0.0696	0.0087
2.81	1.05	6.80	4.85	0.0991	0.0123
2.97	1.10	6.45	4.90	0.1072	0.0133
3.71	1.50	5.85	5.40	0.1539	0.0189
	Slope = 44.9 ± 8.9			$\sigma_1 = 12.3 \pm 2.4$	

Metastable Helium in Oxygen, 30 Electron Volts

$p \times 10^4$	i_+	i_T	i_S	i_+/i_0-i_+	log r
0.06	0.00	7.95	----	0.0000	0.0000
2.42	0.55	4.80	2.70	0.0792	0.0099
3.75	0.95	4.65	3.35	0.1348	0.0167
5.57	1.35	3.55	3.55	0.2350	0.0287
6.55	1.75	3.20	4.50	0.2940	0.0356
7.85	1.75	2.70	4.30	0.3335	0.0401
	Slope = 50.0 ± 5.6			$\sigma_1 = 13.8 \pm 1.5$	

Metastable Helium in Oxygen, 35 Electron Volts

$p \times 10^4$	i_+	i_T	i_S	i_+/i_0-i_+	log r
0.06	0.00	8.05	-----	0.0000	0.0000
2.42	0.60	5.25	2.80	0.0805	0.0100
3.75	1.45	7.15	4.85	0.1374	0.0169
5.57	1.40	3.85	3.65	0.2295	0.0280
6.55	2.50	5.00	6.10	0.2910	0.0352
7.85	2.90	4.90	6.85	0.3280	0.0395
	Slope = 49.5 ± 4.6			$\sigma_i = 13.6 \pm 1.3$	

Metastable Helium in Oxygen, 45 Electron Volts

$p \times 10^4$	i_+	i_T	i_S	i_+/i_0-i_+	log r
0.06	0.00	7.80	-----	0.0000	0.0000
2.42	0.65	5.30	2.70	0.0885	0.0108
3.75	1.60	7.95	5.00	0.1410	0.0174
5.57	1.35	3.90	3.55	0.2210	0.0270
6.55	2.75	5.57	6.40	0.2925	0.0353
7.85	3.10	5.65	6.95	0.3265	0.0393
	Slope = 49.5 ± 4.0			$\sigma_i = 13.6 \pm 1.1$	

Metastable Helium in Carbon Monoxide 30 Electron Volts

$p \times 10^4$	i_+	i_T	i_S	i_+/i_0-i_+	log r
0.06	0.00	7.95	----	0.0000	0.0000
2.28	0.30	5.40	2.60	0.0390	0.0049
4.08	0.50	4.00	3.25	0.0740	0.0092
6.09	1.20	5.15	5.40	0.1284	0.0159
6.22	0.85	3.15	3.60	0.1440	0.0178
8.13	1.20	3.10	4.50	0.1874	0.0230

Slope = 26.4 ± 2.3 $\quad \bar{\sigma}_i = 7.3 \pm 0.6$

Metastable Helium in Carbon Monoxide, 35 Electron Volts

$p \times 10^4$	i_+	i_T	i_S	i_+/i_0-i_+	log r
0.06	0.00	8.05	----	0.0000	0.0000
2.28	0.30	5.60	2.60	0.0380	0.0048
4.08	0.55	4.25	3.35	0.0781	0.0097
6.09	1.40	6.10	6.00	0.1308	0.0161
6.22	0.90	3.40	3.75	0.1440	0.0178
8.13	1.70	4.65	6.15	0.1869	0.0230

Slope = 26.6 ± 1.7 $\quad \bar{\sigma}_i = 7.3 \pm 0.5$

Metastable Helium in Carbon Monoxide, 45 Electron Volts

$p \times 10^4$	i_+	i_T	i_S	i_+/i_0-i_+	log r
0.06	0.00	7.80	----	0.0000	0.0000
2.28	0.35	5.70	2.40	0.0452	0.0057
4.08	0.55	4.30	3.20	0.0792	0.0099
6.09	1.35	6.35	5.75	0.1256	0.0155
6.22	0.90	3.55	3.60	0.1440	0.0178
8.13	1.80	5.25	6.35	0.1837	0.0226

Slope = 26.6 ± 1.4 $\sigma_i = 7.3 \pm 0.4$

Metastable Helium in Nitrogen, 30 Electron Volts

$p \times 10^4$	i_+	i_T	i_S	i_+/i_0-i_+	log r
0.08	0.00	12.30	----	0.0000	0.0000
3.67	0.65	6.75	4.95	0.0589	0.0074
4.92	0.50	2.80	2.20	0.1111	0.0138
6.66	1.10	4.45	5.85	0.1194	0.0148
7.06	1.05	3.90	4.80	0.1373	0.0169
7.47	1.40	4.35	5.80	0.1599	0.0198
8.81	0.75	1.75	2.75	0.2000	0.0245

Slope = 25.1 ± 4.7 $\sigma_i = 6.9 \pm 1.3$

Metastable Helium in Nitrogen, 35 Electron Volts

$p \times 10^4$	i_+	i_T	i_S	$i_+/i_0 - i_+$	log r
0.08	0.00	12.20	----	0.0000	0.0000
3.67	0.65	6.80	4.70	0.0599	0.0075
4.92	0.45	2.70	2.10	0.1034	0.0128
6.66	1.20	5.05	5.60	0.1270	0.0157
7.06	1.10	4.45	4.95	0.1324	0.0164
7.47	1.55	4.80	5.75	0.1722	0.0211
8.81	0.70	1.80	2.55	0.1918	0.0235
	Slope = 25.1 $\pm$ 3.7			$\bar{\sigma}_i$ = 6.9 $\pm$ 1.0	

Metastable Helium in Nitrogen, 45 Electron Volts

$p \times 10^4$	i_+	i_T	i_S	$i_+/i_0 - i_+$	log r
0.08	0.00	11.20	----	0.0000	0.0000
3.67	0.60	6.45	4.30	0.0591	0.0074
4.92	0.40	2.70	1.90	0.0953	0.0118
6.66	1.05	5.05	5.00	0.1167	0.0144
7.06	1.05	4.40	4.40	0.1355	0.0167
7.47	1.40	4.75	5.15	0.1648	0.0203
8.81	0.60	1.80	2.20	0.1765	0.0217
	Slope = 23.9 $\pm$ 3.0			$\bar{\sigma}_i$ = 6.6 $\pm$ 0.8	

Metastable Helium in Hydrogen, 30 Electron Volts

$p \times 10^4$	i_+	i_T	i_S	i_+/i_0-i_+	log r
0.08	0.00	12.30	----	0.0000	0.0000
9.08	0.60	4.70	4.65	0.0686	0.0086
9.84	0.50	4.50	4.45	0.0592	0.0074
12.46	0.65	3.65	4.70	0.0843	0.0105
13.10	0.65	3.30	4.80	0.0873	0.0108
14.52	0.80	3.15	5.00	0.1089	0.0135
15.52	0.85	3.50	5.00	0.1111	0.0138

Slope = 8.7 ± 0.2 $\quad \bar{\sigma}_i = 2.4 \pm 0.1$

Metastable Helium in Hydrogen, 35 Electron Volts

$p \times 10^4$	i_+	i_T	i_S	i_+/i_0-i_+	log r
0.08	0.00	12.20	----	0.0000	0.0000
9.08	0.50	5.20	4.65	0.0534	0.0067
9.84	0.50	4.90	4.65	0.0553	0.0069
12.46	0.70	4.10	4.90	0.0843	0.0105
13.10	0.70	3.75	4.90	0.0880	0.0109
14.52	0.80	3.50	5.10	0.1025	0.0127
15.52	0.80	3.75	5.20	0.0982	0.0122

Slope = 8.0 ± 0.3 $\quad \bar{\sigma}_i = 2.2 \pm 0.1$

Metastable Helium in Hydrogen, 45 Electron Volts

$p \times 10^4$	i_+	i_T	i_S	$i_+/i_0 - i_+$	log r
0.08	0.00	11.20	----	0.0000	0.0000
9.08	0.40	5.00	4.30	0.0449	0.0056
9.84	0.50	4.80	4.35	0.0578	0.0072
12.46	0.65	4.15	4.45	0.0818	0.0101
13.10	0.65	3.80	4.40	0.0861	0.0107
14.52	0.75	3.65	4.70	0.0987	0.0122
15.52	0.70	4.05	4.50	0.0892	0.0111

Slope = 7.6 ± 0.4 $\qquad$ $\tilde{\sigma}_1 = 2.1 \pm 0.1$

BIOGRAPHICAL SKETCH

William Paul Sholette was born in Philadelphia, Pennsylvania, on January 5, 1936. After graduating from Northeast Catholic High School in Philadelphia he entered Saint Joseph's College of the same city, from which he received the Bachelor of Science Degree in June, 1957.

In September, 1957, he entered the Graduate School of the University of Florida. He has since that time held the positions of graduate assistant and Eastman Kodak Fellow in the Department of Chemistry.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 12, 1961

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